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ABSTRACT

Organosolv pulping is attracting increased attention, as a result of its potential suitability for economically adding incremental pulp production capacity, and possible environmental advantages. As yet, however, relatively little research has been done on its fundamental aspects. The purpose of this review is to facilitate further work by summarizing available information on the likely delignification mechanisms operative in major acidic and alkaline organosolv pulping systems. Acidic systems are emphasized, the rationale being that they differ more from conventional processes than do other organosolv processes. Some important reactions in alkaline systems are nevertheless also reviewed. It is concluded that the cleavage of ether linkages is of major importance. Under acidic conditions this is particularly true for α-ethers, but β-ether cleavage also plays a role, especially in hardwood pulping. In alkaline systems, the cleavage of β-ethers is more important. Lignin condensation, a potential limiting factor, can occur in several ways, usually involving reactive carbocation or quinone methide intermediates. Hardwoods are delignified more readily than softwoods, primarily as a result of differences in β-ether reactivity, α-ether concentration, lignin content, and propensity to undergo condensation reactions.

Delignification of wood in nonaqueous media, also known as organosolv pulping, has been the subject of considerable research activity since the idea was introduced early in the century. Much of this activity has occurred in recent years, however, and most has been empirically directed toward identification of efficient solvent systems and optimum process conditions. Until recently, very little work had been done to understand the fundamental aspects of these systems, so little detailed information is available on their mechanisms. On the other hand, the mechanisms of the kraft and sulfite pulping processes and their variants have been studied in detail, and there has been considerable basic work on nonaqueous lignin solvolysis, although most of it has not been primarily directed at understanding the related industrial processes. For example, numerous studies

have been done for the purpose of elucidating lignin structure by analyzing its solvolysis products. As a result, there exists a substantial amount of information which can serve as a basis for inferences concerning organosolv pulping mechanisms. In addition, increased levels of basic research on the subject during the past few years have added to a growing store of theoretical knowledge that should facilitate further development of organosolv pulping technology.

The purpose of this paper is to assist this development by reviewing pertinent information from all three sources: existing knowledge of the chemistry of aqueous pulping systems, lignin solvolysis studies, and recent organosolv pulping research. Emphasis is placed on highlighting the important questions and providing a sampling of the literature dealing with each. Accordingly, no effort has been made to ensure comprehensive coverage of the literature.

The Nature of Organosolv Pulping

Traditional chemical pulping processes depend for their effectiveness on an ability to progressively break down and modify the lignin macromolecule until the resulting molecular fragments become small enough to dissolve in the aqueous pulping liquor. It might be supposed that organosolv pulping, by replacing much or all of the water with an organic solvent, delignifies by physically dissolving lignin without first chemically fragmenting it. In fact, no solvent has been found that can achieve this desirable goal, and all organosolv processes rely on chemical breakdown of the lignin prior to dissolving it.

Numerous studies within the field of lignin chemistry have led to the conclusion that the cleavage of ether linkages is primarily responsible for lignin breakdown in organosolv processes. Easily hydrolyzable α-ether bonds are most readily broken, but it is likely that ß-aryl ether bonds are also broken under the conditions of many processes. Important parameters governing the course of delignification are pH, physical properties of the solvent that govern its ability to dissolve lignin fragments, and chemical properties of the solvent that govern its ability to participate in fragmentation reactions or inhibit lignin recondensation. In the following, significant aspects of these phenomena are reviewed, with emphasis on the chemistry of delignification in acidic and neutral (autocatalyzed) processes.

ACIDIC AND NEUTRAL PROCESSES

As is apparent from recently published reviews,[1,2,3] most of the organosolv processes

use either a neutral solvent, with or without an added acid catalyst, or an acidic solvent. In cases where no acid is added, the liquor becomes acidic as a result of release of acetic acid from the wood. Under these conditions neutral and acid solvolysis reactions of lignin, as reviewed by Wallis[4] and Adler,[5] may be expected to occur.

α-Ether Cleavage

Some of the lignin in wood can be removed simply by heating the wood in water. Nimz,[6] for example, dissolved 40% of the lignin in beech and 10% of that in spruce by treatment with water at 100° C. The responsible reactions, which very likely also occur in organosolv pulping, are believed to consist primarily of the solvolytic splitting of α-ether linkages. Model compound studies[7] have shown that α-aryl ether linkages are more easily split than ß-aryl ether linkages, especially when they occur in a lignin structural unit containing a free phenolic hydroxyl group in the para position. In this case the formation of a quinone methide intermediate is possible, as shown in **Figure 1**. Otherwise, a nucleophilic substitution reaction occurs at the benzylic position by an S_N2 mechanism (**Figure 2**).

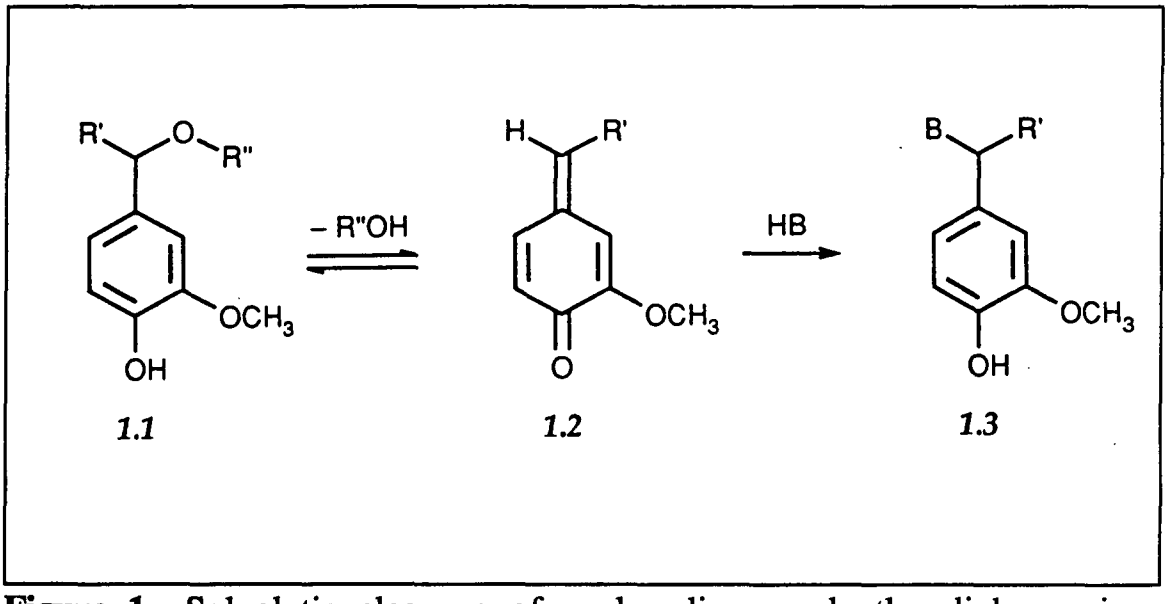

Figure 1 Solvolytic cleavage of a phenolic α-aryl ether linkage via a quinone methide intermediate. B = OH, OCH_3 etc.

In the presence of added acid, the hydrolysis of benzyl ether linkages is facilitated by acid catalysis (**Figure 2**). It is also possible for the ether linkage to be directly broken, with the formation of a resonance-stabilized benzyl carbocation, as shown in **Figure 3**. This reactive intermediate may undergo undesirable condensation reactions with other units.

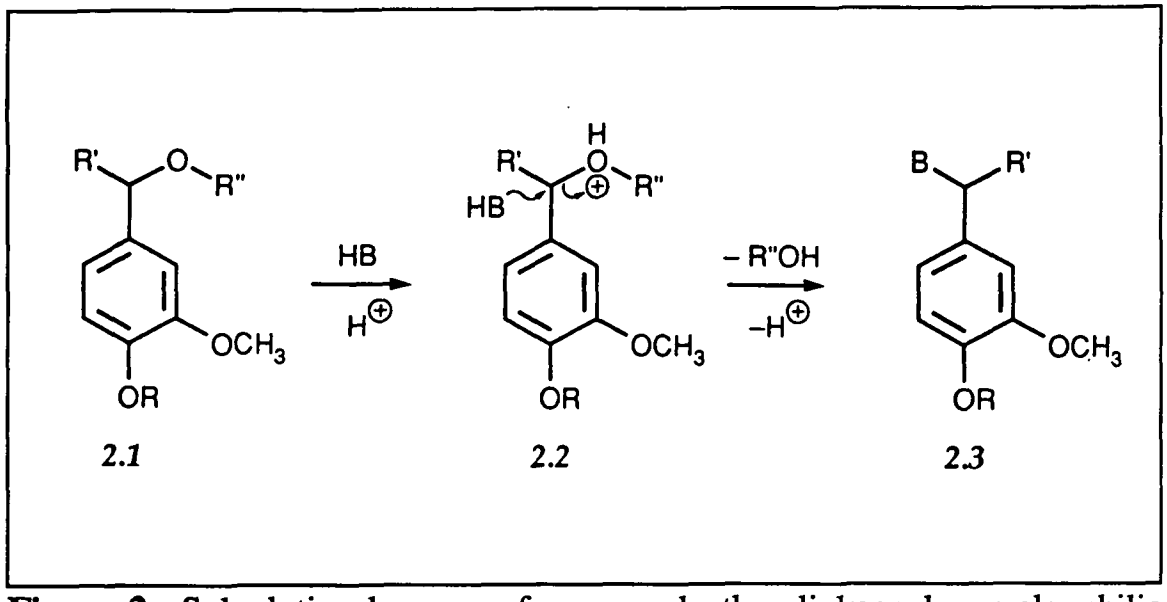

Figure 2 Solvolytic cleavage of an α-aryl ether linkage by nucleophilic substitution. R = H or CH_3; B = OH, OCH_3, etc.

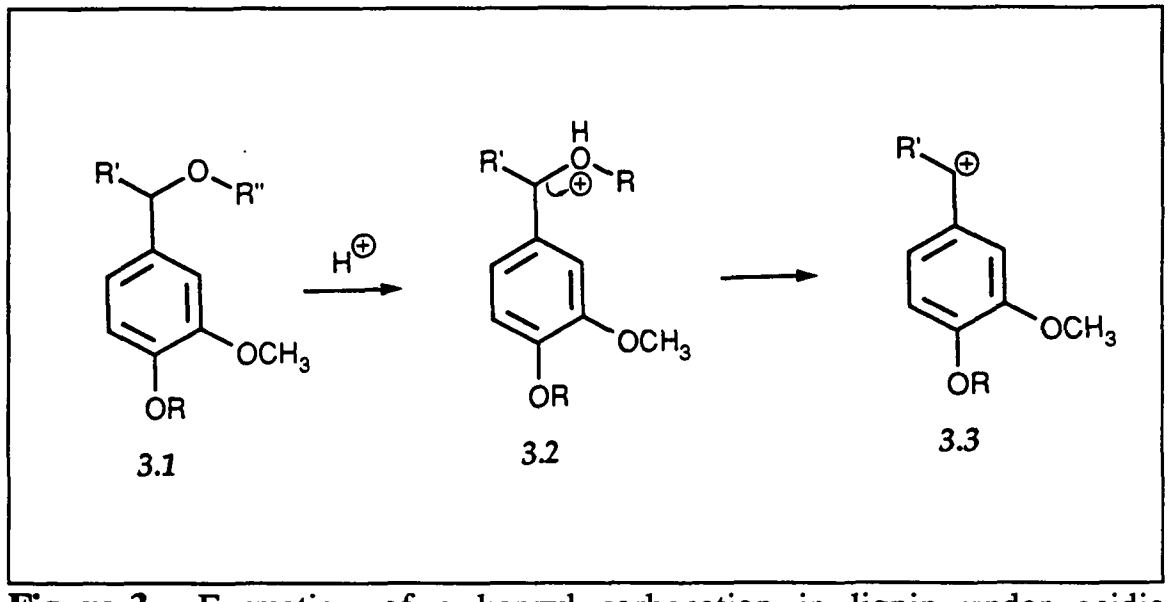

Figure 3 Formation of a benzyl carbocation in lignin under acidic conditions. R = H or CH_3

ß-Ether Cleavage

Hydrolysis with water is believed to involve cleavage of α-ethers as the predominant, and perhaps the only reaction. The cleavage of ß-ethers cannot be ruled out, however. Sano[8] studied the hydrolysis, in 1:1 dioxane-water, of a dimeric model compound containing a ß-aryl ether linkage and observed the formation of products that they explained in terms of breakage of this bond by a homolytic (free-radical) mechanism. It is nevertheless probable that α-ether cleavage occurs to a much greater extent.[5]

The likelihood of ß-ether cleavage is greater in more strongly acidic systems. When spruce milled wood lignin is refluxed with 0.2M HCl in 9:1 dioxane-water, the products include several carbonyl compounds having the guaiacyl propane carbon skeleton.[9] By analogy with compounds obtained by Hibbert's group[10] upon ethanolysis of spruce wood, these compounds are called Hibbert's ketones. The same compounds are also obtained when the model compound, guaiacylglycerol-ß-guaiacyl ether (protonated form, *4.1*) is refluxed with dioxane-water containing HCl,[11] showing that they result from

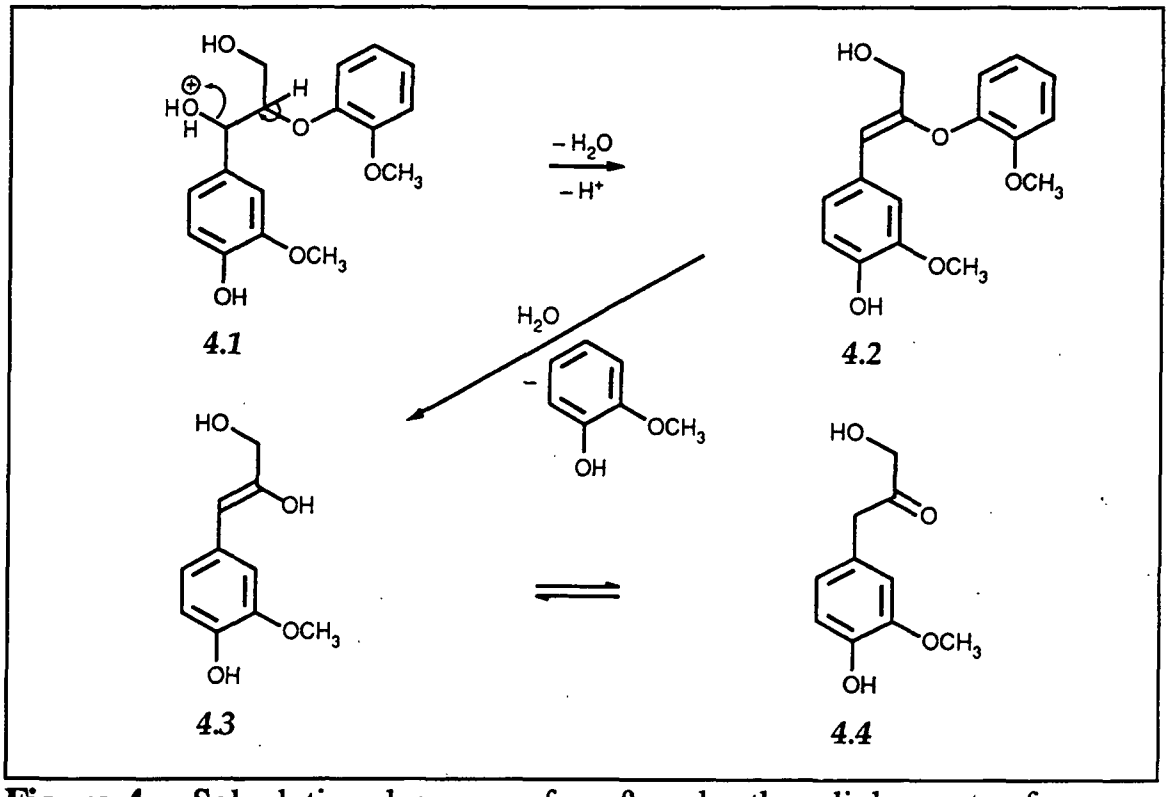

Figure 4 Solvolytic cleavage of a ß-aryl ether linkage to form ω-guaiacylacetone

cleavage of the ß-ether linkage, as shown in **Figures 4 and 5**. Formation of either a

resonance-stabilized benzyl carbocation or a similarly stabilized transition state is followed by elimination of water to form the readily hydrolyzed enol ether, *4.2*. This releases guaiacol and forms ß-hydroxyconiferyl alcohol (*4.3*), which exists in equilibrium with its keto form, ω-hydroxyguaiacylacetone (*4.4*). Allylic rearrangement of the side chain then gives the enediol which is an equilibrium mixture of *5.3, 5.4, 5.5,* and *5.6,* as well as the α,ß-diketone and ß-ketone that result from disproportionation of *5.4*.

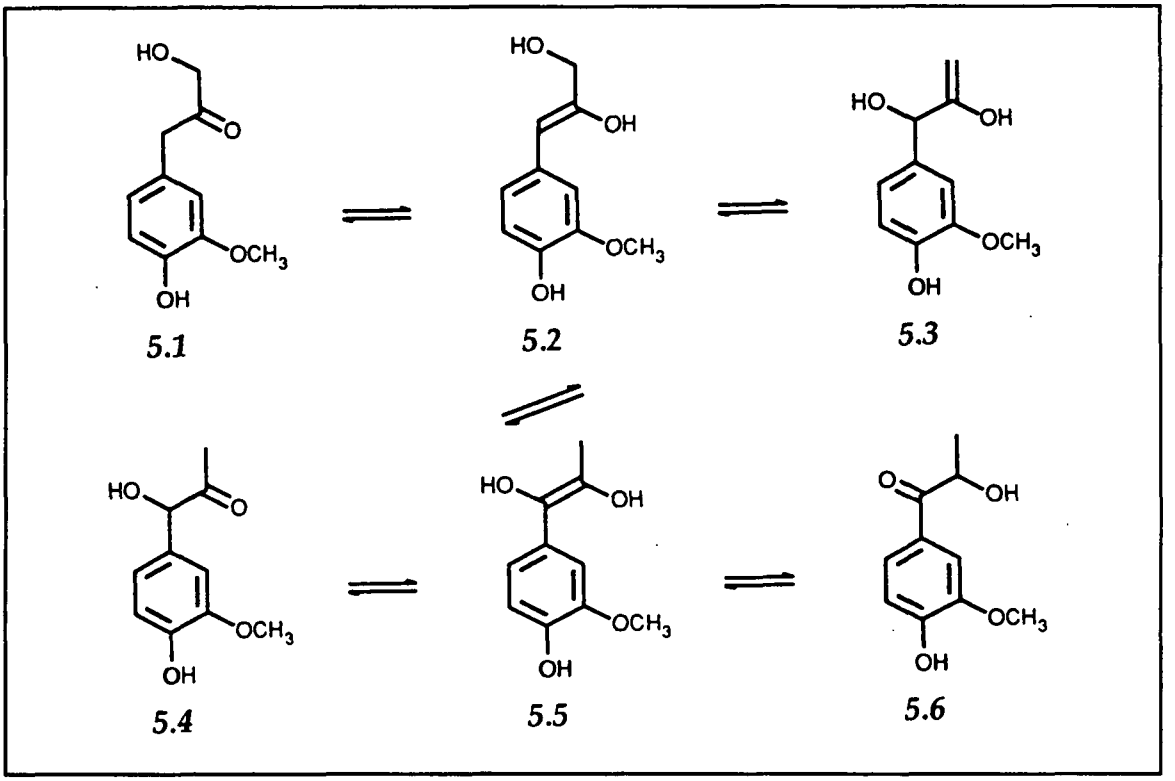

Figure 5 Formation of Hibbert's ketones following ß-ether cleavage

The significance of this in the present context is that the occurrence of Hibbert's ketones (*5.4, 5.6,* and the disproportionation products) in a spent pulping liquor may be taken as an indication of ß-ether cleavage according to the scheme shown in **Figure 4**. In fact, however, attempts to find these ketones in the spent liquors of autocatalyzed organosolv pulping processes have failed to result in the detection of more than trace amounts.[3,12] This has been interpreted as suggesting that ß-ether cleavage does not play a significant role in such processes. Sarkanen, in espousing this view, has pointed out that acidolysis of isolated organosolv lignins increases substantially the content of phenolic hydroxyl groups, indicating the presence of intact ß-O-4 bonds, and that the activation energy of organosolv delignification, 8.4 kcal/mol, is much lower than the value of 36 kcal/mol obtained for the hydrolysis of ß-aryl ether bonds.[3]

The opposing view, that ß-ether cleavage is an important component of the organosolv pulping mechanism, has also been expressed and supported with experimental evidence. Thus, Gallagher *et al.*[12] interpreted a large increase in the phenolic hydroxyl content of lignin upon autocatalyzed ethanol-water organosolv delignification as being indicative of rather extensive ß-ether cleavage. A partial resolution of these conflicting views may be found in the possibility that ß-ether bonds may be broken by other mechanisms than the one represented in **Figure 4**, thus accounting for the failure of significant quantities of Hibbert's ketones to appear. For example, loss of the γ-methylol group as formaldehyde is another pathway available to the ß-ether linked structural grouping or its carbocation.[13] As shown in **Figure 6**, the resulting enol ether is subsequently

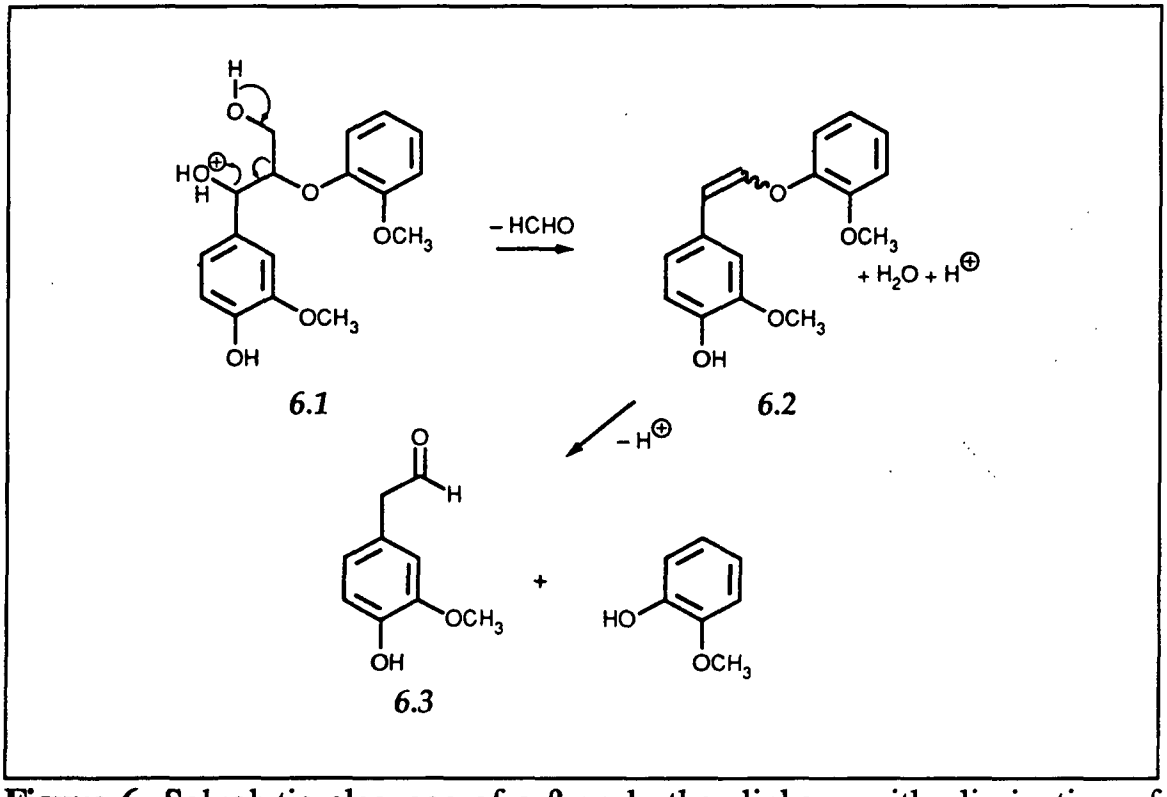

Figure 6 Solvolytic cleavage of a ß-aryl ether linkage with elimination of formaldehyde

hydrolyzed, the end result being breakage of the ether bond. Indeed, Gallagher *et al.*[12] have observed a substantial loss of aliphatic hydroxyls, as would be expected to accompany loss of terminal methylol groups.

If the pathway shown in **Figure 6** is accepted as a possible route, Sarkanen's remaining objections might be dealt with by postulating the existence of a rate determining step other than ß-ether cleavage, such as diffusion, and by admitting that the hydrolysis of ß-

ether bonds is not complete, leaving some to serve as the source of new phenolic hydroxyl groups in a subsequent acidolysis experiment.

Other mechanisms for ether cleavage may also be available. Sano, for example, has obtained evidence suggesting that ß-ether linkages in model compounds are broken in dioxane-water[8] and p-cresol water[14] by homolytic processes.

In more strongly acidic systems, the occurrence of ß-ether cleavage may be more extensive. One reason is that these systems bear a greater resemblance to the classical acidolysis systems in which the breakage of ß-ethers has been established. In addition, several studies have provided evidence that these reactions occur under pulping conditions. Lai and Guo,[15] for example, measured the rate of liberation of phenolic hydroxyl groups in the treatment of spruce and aspen with 0.1M HCl in water, 50% aqueous ethanol and 50% aqueous ethylene glycol. After finding similar results in all three media they used the aqueous medium to demonstrate extensive ß-ether cleavage in aspen at 130°C. Spruce, however, did not respond similarly. Nimz and Robert,[16] on the other hand, used[13] C NMR spectroscopy to compare milled wood lignin with lignin obtained from spruce wood chips by treatment with 95% aqueous acetic acid containing 0.1% hydrogen chloride. The latter was observed to be enriched in phenolic hydroxyl groups and to exhibit changes in the aliphatic region of the spectrum that were consistent with ß-ether cleavage.

Model compound studies of organic acid pulping also support the view that ß-ether cleavage occurs in these systems. Shimada, Hosoya and Tomimura[17] showed that concentrated aqueous solutions of propionic, acetic, or formic acids liberated guaiacol from guaiacylglycerol- and veratrylglycerol-ß-guaiacyl ethers, propionic acid being more effective than acetic and formic being the least effective. Ede *et al.*[18] reacted the same model compounds with 85% formic acid and detected 20-24% ß-ether cleavage. They also provided evidence that this number would have been higher if ß-ether cleavage had not been inhibited by formylation of the γ-methylol group. Blocking of this group prevents ether cleavage by the mechanism shown in **Figure 6.**

The length of the above discussion reflects the potential importance of ß-ether cleavage as a delignification mechanism. In summary, it appears that reactions of this type occur in autocatalyzed and acid catalyzed organosolv pulping processes, but to an extent that may be limited by the characteristics of the particular process. In general, ß-ether cleavage is likely to be more important in those processes that are more strongly acidic, and more important in the pulping of hardwoods than in the pulping of softwoods. Its occurrence may be limited by solvent-specific reactions, such as the formylation of primary alcohol groups.

Cleavage of Lignin-Carbohydrate Bonds

It is generally observed that organosolv lignins have low carbohydrate contents, suggesting that the bonds anchoring lignin to hemicellulose in wood are readily hydrolyzed under acidic conditions. This is in accord with the hypothesis that these bonds consist of ether linkages between the carbohydrate and the α-carbon atoms of lignin sidechains, since such bonds are known to be readily hydrolyzed.[3]

Lignin Condensation Reactions

The formation of intermolecular bonds between lignin fragments is obviously a counterproductive process if lignin must be depolymerized to be removed from the cell wall. This is doubly true if the bonds are formed between carbon atoms, since few pathways are available for breaking such bonds. On the other hand, a prominent pathway for their formation is suggested by formation of the carbocation, as shown in **Figure 3**, since this ion can readily form a bond with an electron-rich carbon atom in the aromatic ring of another lignin unit. In less strongly acidic systems, protonation of a benzyl-linked oxygen atom may also facilitate condensation by processes of the S_N2 type.

Condensation at the α position of the side chain can be readily illustrated by reactions of lignin model compounds. Ede and Brunow,[19] for example, obtained high yields of the condensation product *7.3* by reacting a veratrylglycerol-ß-guaiacyl ether derivative (*7.2b*) with propylveratrole (*7.1*) in refluxing 85% formic acid (**Figure 7**). Note that *7.3* is unable to undergo ß-ether cleavage because of the unavailability of an α-hydroxyl to serve as a leaving group, so its formation represents an irreversible condensation process. Evidence of the importance of such reactions had been provided in an earlier study by the same authors.[18] When *7.2a* was subjected to the same reaction conditions, but in the absence of *7.1*, the resulting product mixture gave NMR spectra indicative of the occurrence of intermolecular condensation reactions. Furthermore, the yields of vanillin and syringaldehyde obtained upon nitrobenzene oxidation of the dissolved lignin decrease with increasing cooking time when wood is pulped with organic acids[17] indicating that lignin condensation occurs during cooking.

Intramolecular condensation is also likely to play a role during pulping. Prominent among the products obtained from *7.2a* in refluxing formic acid was the aryldihydrobenzofuranmethanol formate ester *7.4*.[18] This reaction is of dual significance. Although it precludes ß-ether cleavage, it also serves to protect the reactive benzylic position from participation in intermolecular condensation.

This protective effect may be operative during solvolysis pulping with phenols.

Sakakibara *et al.*[20] have proposed that benzyl carbocations may react with phenolic solvents by electrophilic aromatic substitution on the aromatic ring of the solvent. This would block the reactive benzyl position, preventing it from undergoing counterproductive intermolecular condensation reactions with other lignin fragments. Accordingly, Sano *et al.*[21] have observed extensive solvent incorporation into cresol solvolysis lignins. More recently, however, Sano has conducted model compound studies suggesting that these ionic reactions are less important than free radical reactions in phenol pulping systems,[14] and that the principal role of the phenols is to trap lignin radicals and other reactive intermediates before they can condense. In Sano's view, low molecular mass phenol lignins are produced mainly by the homolysis of p-hydroxyarylglycerol-ß-aryl ethers in lignin.

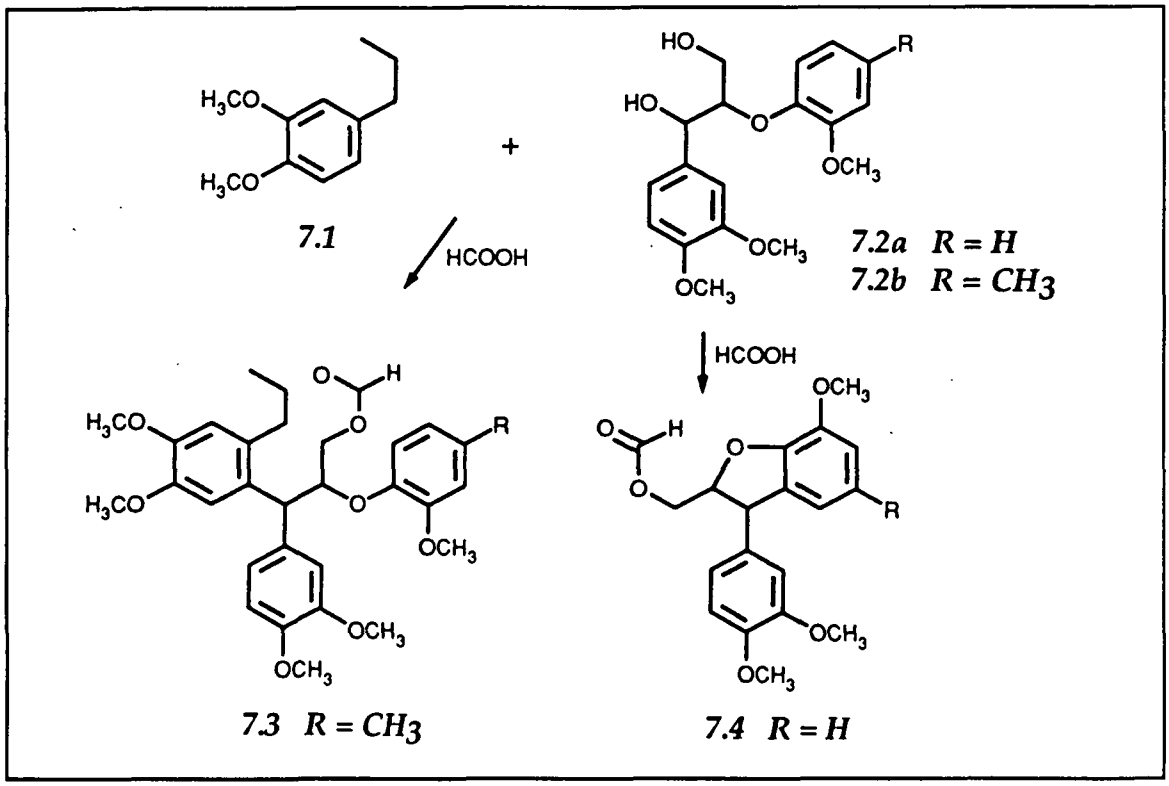

Figure 7 Inter- and intramolecular condensations of lignin model compounds in formic acid

Because lignin condensation accompanies the formation of the benzylic carbocation (or protonation of a benzylic oxygen atom), it is more likely to occur as the acidity of the system is increased. Accordingly, it has been observed[17] that condensation during pulping of wood occurs to a greater extent with formic acid than with acetic acid, and to a greater extent with acetic acid than with propionic acid. This conclusion was based on aldehyde yields in nitrobenzene oxidation and on gel permeation chromatography of milled wood

lignin after treatment with the acids. Propionic acid was also observed to delignify more effectively than either of the other two acids.

In spite of the model compound results discussed above, the importance of condensation reactions in organosolv pulping remains difficult to assess. Some experimental results suggest that they do not play a large role. Thus, Gallagher *et al.*[12] have estimated, on the basis of NMR spectroscopy of ethanol-water lignin, that the fraction of guaiacyl units that are condensed is only slightly greater than in milled wood lignin (35% vs. 30%), in contrast to the 54% estimated for methanol-HCl lignin. Tirtowidjojo *et al.*[22] added isolated organosolv lignin to pulping solvent (0.01MH_2SO_4 in 70:30 v/v MeOH-H_2O) in an amount sufficient to give a fourfold increase in lignin concentration during the reaction and detected no effect on the residual lignin content of the resulting pulp. On the other hand, it is commonly observed that the yield of aldehydes from nitrobenzene oxidation of the dissolved lignins decreases with increased cooking time.[17,21,23] Furthermore, in organic acid pulping, aldehyde yield correlates with delignification effectiveness and (inversely) with lignin molecular mass.[17] In summary, it appears that a variety of pathways for lignin condensation are available, and that the extent to which they become practically significant depends on the acidity of the system and perhaps on other factors which are not as yet clearly understood.

Hardwood-Softwood Differences

It was recognized very early in the investigation of organosolv pulping processes that, in general, hardwoods are delignified faster and more selectively than softwoods. Although this can be partly explained on the basis of the higher lignin contents of softwoods, the magnitude of the differences in pulping behavior suggest that other factors are also involved. Sarkanen[3] postulated that one of these is a higher content of easily hydrolyzed α-ether linkages in hardwoods, as indicated by their greater acid-soluble lignin contents, and that another is the greater tendency of softwood lignins to undergo intermolecular condensation reactions. Subsequently, Lai and Guo[15] have shown that, in comparison to spruce, aspen lignin contains 50% more noncyclic α-aryl ether structures, but also that it contains a high proportion of ß-aryl ether units with hydrolysis rates substantially higher than those of norway spruce. The latter finding may provide the key to understanding the behavior of hardwoods in organosolv as well as other pulping processes.

The role of condensation reactions is, once again, unclear. Model compound studies by Shimada *et al.*[17] showed that in condensation reactions of benzyl carbocations with anionic aromatic ring sites, the reactivities of guaiacyl carbocations were higher than those of syringyl ones, suggesting that higher rates of lignin condensation may be partially

responsible for the slower softwood delignification rate. On the other hand, the same workers also showed that the anionic centers in syringyl rings are more reactive than those in guaiacyl rings.

ALKALINE PROCESSES

Organosolv pulping in alkaline systems is less distinct from conventional processes than are the autocatalyzed and acidic organosolv processes. Unlike the latter, the alkaline systems would remain viable pulping processes, albeit possibly less effective, if the nonaqueous component were omitted. Thus, alkaline sulfite anthraquinone methanol (ASAM) pulping has a more conventional counterpart in the alkaline sulfite anthraquinone (ASAQ) process and soda-anthraquinone-methanol pulping is enhanced by, but not totally dependent on, the presence of methanol. By the same token, the principal mechanisms involved are probably similar to those of the parent aqueous processes. On the other hand, one cannot be certain of this, since relatively little research effort has been devoted to the fundamentals of the ASAM and soda-alcohol processes. Some potentially important alkaline reactions of lignin are reviewed here. Others, including some likely to be important during ASAM pulping, have been reviewed by Gierer.[24]

α-Ether Cleavage

Ionization of a free phenolic hydroxyl group facilitates its conversion to a quinone methide in alkaline medium, provided that a suitable leaving group is situated at the α-position of the side chain (**Figure 8**). If this α-substituent is the aroxy group of an adjacent lignin structural unit (not also connected through the ß-position) fragmentation of the lignin macromolecule results.[25] Units containing only etherified phenolic hydroxyl groups cannot undergo conversion to quinone methides and are not subject to α-ether cleavage by this route.

ß-Ether Cleavage

ß-ethers can be cleaved in alkaline medium regardless of whether the phenolic hydroxyl group on the associated ring is free or etherified. In the case of etherified units, the pathway shown in **Figure 9** is available.[25] An ionized hydroxyl group serves as a nucleophile in displacing the neighboring aroxy substituent, with the formation of an oxirane ring, which is subsequently opened to form a glycol grouping.

In the case of units bearing free phenolic hydroxyl groups, initial cleavage of an α-ether

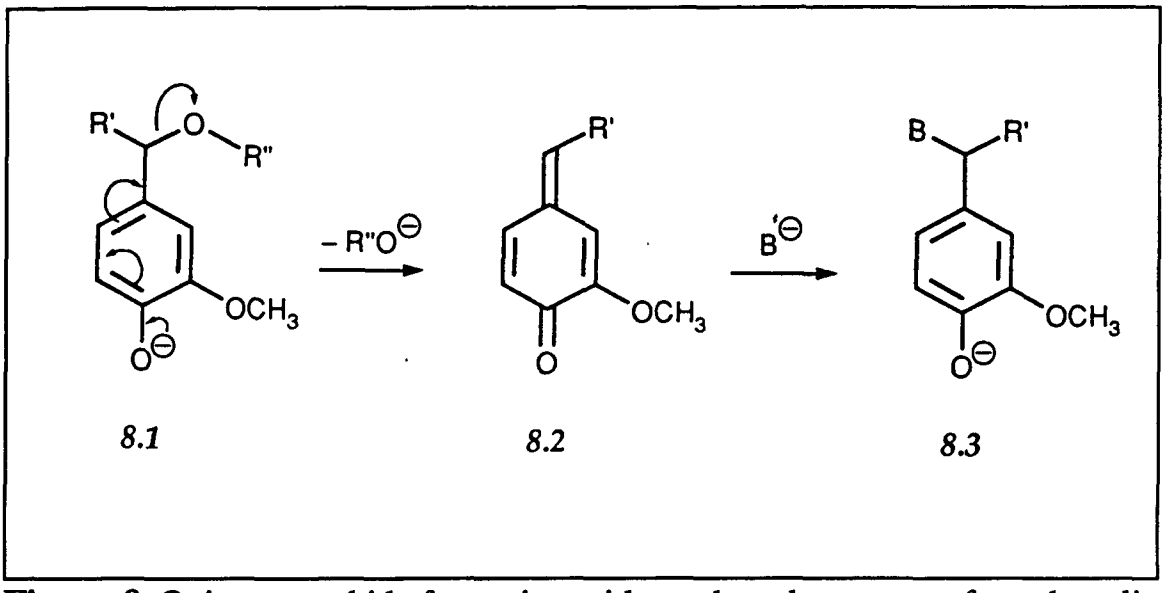

Figure 8 Quinone methide formation with α-ether cleavage on free phenolic units

linkage may be followed by nucleophilic addition of hydroxide ion to the resulting quinone methide at the α-position, and then by displacement of the neighboring ß-ether substituent, as shown in **Figure 9**. Alternatively, if hydrosulfide is present, the same sequence could occur, with the sulfur atom playing the role played by the oxygen atom at the α-position in **Figure 9**.[26] A third possibility is that anyhrahydroquinone, or a related compound might serve the same function either by forming an adduct[27] or by direct electron transfer.[28] Other potentially important reactions in an alkaline anthraquinone system have been reviewed by Schroeter.[29]

Condensation Reactions

Among the nucleophiles competing for lignin quinone methides in alkaline media are phenolate anions. Because of resonance-related delocalization of their negative charge, phenolate ions also behave as carbanions, with high electron density at positions ortho- and para- to the ionized phenolic hydroxyl group. Addition to a quinone methide therefore may result in the formation of a carbon-carbon bond between one of these ring positions and the α-sidechain position of another unit. This reaction is irreversible and therefore represents a counterproductive increase in the size of the lignin molecule.

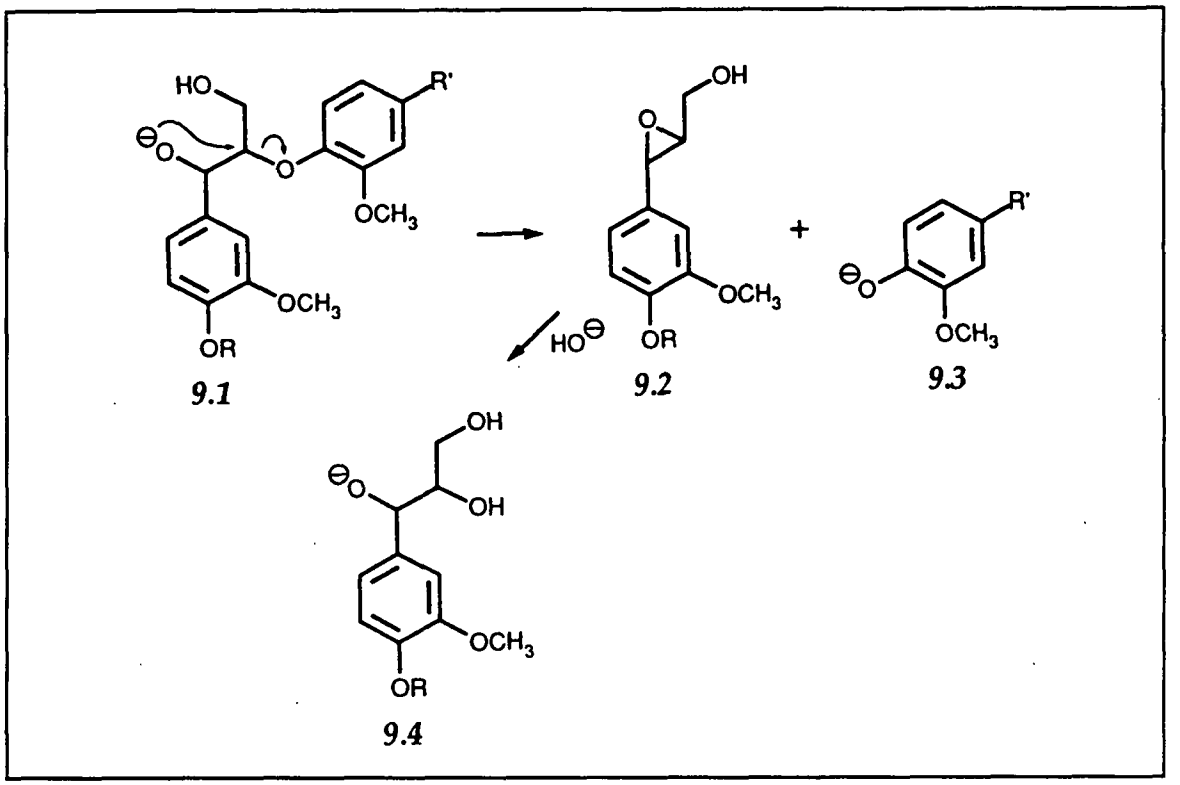

Figure 9 ß-ether cleavage in alkaline medium; R = H or CH_3

SUMMARY AND CONCLUSIONS

1. Organosolv processes rely on chemical breakdown of the lignin macromolecule before it is dissolved. Cleavage of ether linkages is primarily responsible for lignin breakdown.

2. In acidic systems, easily hydrolyzable α-ether linkages are most readily broken, but it is likely that ß-aryl ether bonds are also broken under the conditions of many processes. In general, ß-ether cleavage is likely to be more important in those processes that are more strongly acidic, and more important in the pulping of hardwoods than in the pulping of softwoods. Its occurrence may be limited by solvent-specific reactions, such as the formylation of primary alcohol groups. Acidic organosolv pulping is facilitated by the hydrolysis of ether linkages between lignin and carbohydrate.

3. In alkaline systems, α-ethers are readily cleaved if they occur in units containing free phenolic groups, but not otherwise. Alkaline cleavage of ß-ethers also occurs, especially in the presence of nucleophilic additives such as hydrosulfide ion or an anthraquinone derivative.

4. Lignin condensation is a potentially important counterproductive process in both acidic and alkaline systems. In the former, it results in part from the formation of reactive benzyl carbocations or protonation of a benzyl-linked oxygen atom, both processes being favored by high acidity. Intramolecular condensation may also occur. It has the undesirable effect of precluding subsequent ß-ether cleavage, as well as the desirable effect of preventing intermolecular condensation, at the affected site. By appropriate choice of solvent, the latter effect can be achieved without precluding ß-ether cleavage. Thus, in the phenol pulping processes, benzyl carbocations probably are "protected" by electrophilic aromatic substitution on (condensation with) the aromatic ring of the solvent. Similar reactions are possible in alkaline systems where, however, the reactive intermediate is the quinone method instead of the carbocation.

5. Virtually all organosolv systems delignify hardwoods more readily than softwoods. Although this can be partially explained on the basis of lignin content differences, more important factors are higher ß-ether reactivity and higher concentration of readily hydrolyzable α-ether linkages in hardwood lignin. A reduced tendency of hardwood lignin to undergo condensation reactions may also play a role.

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